National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2660a

Total Oxides of Nitrogen (NO_X) in Air

(Nominal Amount-of-Substance Fraction - 100 μmol/mol)

This Standard Reference Material (SRM) is a primary gas mixture to which the amount-of-substance fraction, expressed as concentration [1], of secondary standards may be related. This SRM may also be used for the calibration of instruments used for total oxides of nitrogen (NO_X) determinations, for monitoring source emissions, and for other applications including the analysis of chemical and combustion process streams.

This SRM mixture is supplied in a DOT 3AL specification aluminum (6061 alloy) cylinder with a water volume of 6 L. Mixtures are shipped with a nominal pressure exceeding 12.5 MPa (1800 psi) which provides the user with 0.73 m^3 (25.8 ft^3) of useable mixture. The cylinder is the property of the purchaser and is equipped with a CGA-660 stainless steel valve which is the recommended outlet for nitric oxide mixtures. NIST recommends that this cylinder not be used below 0.8 MPa (100 psi).

Certification: This SRM mixture has been certified for the total oxides of nitrogen (NO_x) concentration which is defined as the sum of the nitrogen dioxide (NO_2) concentration plus the contaminant gaseous nitric acid (HNO_3) concentration. The certified value given below applies to the identified cylinder and NIST sample number.

Total Oxides of Nitrogen (NO_x) = μmol/mol ± 1.0 μmol/mol

Cylinder Number: NIST Sample Number:

The uncertainty of the certified value includes the estimated uncertainty of the gravimetrically calibrated permeation gas standards, the imprecision of measurements intercomparing the primary standards to the lot standard, and the imprecision of intercomparing the lot standard with each of the mixtures comprising the lot. The uncertainty is expressed as an expanded uncertainty $U = ku_c$, with u_c being determined from experimental standard deviations and the coverage factor k equal to 2. Since the concentration values of NIST gaseous SRMs are assumed to be normally distributed with an experimental standard deviation of u_c, the true concentrations are asserted to lie in the interval defined by the certified value ± U with a level of confidence of approximately 95 % [2].

Expiration of Certification: The certified value is valid until **30 July 2005** within the measurement uncertainties specified, provided the SRM is handled and stored in accordance with the instructions given in this certificate. However, the certification will be nullified if the SRM is contaminated or modified.

Cylinder and Gas Handling Information: NIST recommends the use of a high purity, stainless steel, two-stage pressure regulator with a stainless steel diaphragm and CGA-660 outlet to safely reduce the pressure, and to deliver this SRM mixture to the instrument. The regulator should be evacuated and purged several times to prevent accidental contamination of the sample.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by J.C. Colbert.

Willie E. May, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 24 November 1999

Thomas E. Gills, Director
Office of Measurement Services

The analytical measurements leading to the certification of this current SRM lot were performed by P.M. Chu, M.E. Kelley, and W.J. Thorn III of the NIST Analytical Chemistry Division.

The overall direction and coordination of the technical work required for the certification of this SRM were performed by F.R. Guenther of the NIST Analytical Chemistry Division.

Mixture Preparation: The gas mixtures comprising this SRM lot were prepared in accordance with NIST technical specifications for their preparation by a commercial specialty gas vendor under contract to NIST. The specifications stipulate that each SRM mixture be similar in total NO_x concentration and stable with time.

Analytical Methods: Analysis of the total oxides of nitrogen (NO_x) concentrations were conducted by intercomparing each cylinder mixture to a representative cylinder chosen from the lot, the lot standard (LS), using a chemiluminescent continuous analyzer equipped with a 750 °C thermal converter. Assignment of the NO_x concentration to the lot standard was accomplished by intercomparison of dynamically generated permeation standards using chemiluminescence.

Homogeneity Analysis: Each of the NO_x mixtures which comprise this SRM lot was compared to the LS using thermal disassociation and chemiluminescence. An analysis of variance indicated that sample-to-sample NO_x ratio differences were statistically significant. This indicates that the lot is non-homogeneous and that individual total NO_x concentrations are assigned to each SRM cylinder in this lot.

Total Oxides of Nitrogen (NO_x) Concentration Value Assignment: The certified total oxides of nitrogen concentration for each cylinder in this SRM lot was computed from the assigned NO_x concentration for the lot standard, and the measured NO_x chemiluminescence ratio of this SRM to the lot standard.

Estimate of Gaseous Nitric Acid (HNO_3) Contamination of Total NO_x: Nitric acid (HNO_3) has been found to be ubiquitous in cylinders containing NO_2 in air mixtures. An estimate of the gaseous HNO_3 contamination level in this SRM 2660a lot was determined by Fourier transform-infrared spectroscopy (FT-IR) on a 20 % statistical sub-lot (9 cylinders). An average value of 2.6 μmol/mol ± 0.8 μmol/mol HNO_3 was assigned to this SRM 2660a lot; with the balance of the NO_x comprising nitrogen dioxide (NO_2). This estimate is not a NIST certified value, but is presented here for user information purposes only.

Verification of Air Matrix Composition: The air matrix in SRM 2660a closely matches ambient air, containing oxygen, argon, and carbon dioxide. Two mixtures from the lot were analyzed on a quadrapole mass spectrometer to verify matrix composition. The samples were found to contain 20.8 % mol/mol ± 0.4 % mol/mol oxygen, 0.98 % mol/mol ± 0.09 % mol/mol argon, and 350 μmol/mol ± 70 μmol/mol carbon dioxide with the balance being nitrogen. These values are not NIST certified concentrations but are presented here for user information purposes only.

Stability: Periodic analyses of units from SRM lots are performed at NIST to monitor the stability. If significant changes in the total oxides of nitrogen (NO_x) concentration are observed, the purchaser will be notified. Refer to the Cylinder and Gas Handling Information section for proper handling of this SRM.

REFERENCES

[1] Taylor, B.N., "Guide for the Use of the International System of Units (SI)," NIST Special Publication 811, 1995 Ed., (April 1995).

[2] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed. ISO. Geneva, Switzerland, (1993): see also Taylor, B.N. and Kuyatt, C.E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Technical Note 1297, U.S. Government Printing Office, Washington DC, (1994); (available at http://physics.nist.gov/Pubs/).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: Telephone (301) 975-6776 (select "Certificates"), Fax (301) 926-4751, e-mail srminfo@nist.gov, or via the Internet http://ts.nist.gov/srm.